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Sonochemical enhancement of hydrogen peroxide production by inert glass beads and TiO_2-coated glass beads in water

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ABSTRACT

In this study, a series of experiments were carried out to determine the effects of ultrasound frequency at 28, 580, and 1000 kHz on H_2O_2 production in the presence of both inert and TiO_2-coated glass beads. Several different sizes (no addition, 0.05, 0.1, 1, 2, 3, and 5 mm) and amounts (no addition, 10, 25, 50, 100, and 200 g L^{-1}) of inert glass beads were tested at a power density of 0.2 W mL^{-1}. The production of H_2O_2 with a contact time of 60 min at different frequencies follows the order: 580 kHz (339 μM/no addition–105 μM/2 mm) > 1000 kHz (208 μM/no addition–4.0 μM/1 mm) > 28 kHz (71.2 μM/0.1 mm–18.5 μM/no addition). For a constant glass-bead size of 0.1 mm and at a frequency of 28 kHz, the zero-order rate constant is highest in the presence of glass beads of the amount 10 g L^{-1} (3.3 μM^{-1} min^{-1}), and it decreases significantly with increasing inert glass-bead amounts (2.7 μM^{-1} min^{-1}/25 g L^{-1} to 0.45 μM^{-1} min^{-1}/200 g L^{-1}). The zero-order rate constant is the lowest (0.31 μM^{-1} min^{-1}) with no addition of glass beads. Sonocatalysis at a low frequency of 28 kHz with the addition of TiO_2-coated glass beads (5 mm) of amount 100 g L^{-1} was significantly more effective (1540 μM) than sonocatalysis carried out with no addition and inert glass beads (12–18 μM) and those carried out at the high frequencies of 580 kHz (33.4 μM) and 1000 kHz (8.77 μM), with the other conditions remaining the same.

1. Introduction

The sonochemical process has been found to be an attractive advanced technology for the elimination of contaminants in water [1–4]. Sonochemical degradation has significant advantages such as safety, cleanliness, and energy conservation; moreover, it does not cause secondary pollution [5,6]. It is well known that the sonolysis of water produces hydrogen peroxide (H_2O_2) via hydroxyl and hydrogen radicals. Sonochemical reactions associated with $OH^\bullet$ from cavitation bubbles have good potential for effectively remove contaminants in water, and thus, are promising for wastewater treatment. Cavitation, which includes nucleation, growth, and collapse of small gas bubbles in liquids, is the basis of four theories, namely, the hot-spot, electrical, plasma discharge, and supercritical theories [7–9]. These theories have led to the proposal of several modes of reactivity: pyrolytic decomposition, hydroxyl radical oxidation, plasma chemistry, and supercritical water oxidation [7].

Among advanced oxidation processes such as sonocatalysis, ozone/H_2O_2, UV/H_2O_2, UV/TiO_2, and Fenton/photo-Fenton, sonocatalysis is a relatively new and efficient technique for degrading contaminants; however, it has attracted considerable attention for water and wastewater treatment [10–19]. A direct production of H_2O_2 (<120 μM) was achieved in a catalytic membrane contactor [20]. The photo-Fenton reaction produces a concentration of <1.2 μM H_2O_2 in the presence of fulvic acid [21]. Microbially driven Fenton reaction that produces H_2O_2 (<40 μM) degrades pentachlorophenol from water [22]. H_2O_2 photochemical production measured in bulk and size-fractionated surf zone and source waters ranged from <2 to 10 μM [23]. However, H_2O_2 production (∼200 μM) has been enhanced during sonolysis and/or sonocatalysis in previous studies [24,25]. With regard to the mechanisms of TiO_2 sonocatalysis, previous studies have indicated that TiO_2 sonocatalysts irradiated with ultrasonic sound waves create a synergistic effect that enhances the degradation of contaminants as a result of the highly reactive free radicals such as $OH^\bullet$, $H^\bullet$, and $OH_2^\bullet$. These supplementary radicals are generated by the electron–hole couples created by excitation of TiO_2 particles with ultrasonic irradiation [26]. The presence of TiO_2 particles contributes to an increase in bubble cavitation that promotes the transfer of the generated free radicals to the liquid bulk region as the bubble collapses [27]. In other studies, the presence of a heterogeneous catalyst appears to increase the formation rate of cavitation bubbles by providing additional nuclei, which increase the pyrolysis of H_2O molecules and the formation of $OH^\bullet$ [28,29].

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The practical restriction in the use of catalyst powder in an ultrasonic reactor for sonodegradation involves the separation of the fine catalyst powder from the treated water. Therefore, various supporting materials such as glass beads, silica, alumina, ceramics, zeolites, and magnesia are employed to immobilize powder catalysts for photodegradation and/or sonodegradation of the contaminants [10,17,26,30–33]. Among the several semiconductors employed, the anatase phase of TiO_2 is the most preferable material for photocatalytic treatment due to its high photosensitivity, harmless properties, large bandgap, and stability [34,35]. An assumption can be made that ultrasonic irradiation over a TiO_2 catalyst using TiO_2-coated glass beads would enhance the generation of $OH^\bullet$ and this effect is mediated by similar mechanisms as TiO_2 photocatalysis.

The generation of $OH^\bullet$ associated with H_2O_2 has been documented in TiO_2-coated glass bead sonocatalytic or photocatalytic systems at different ultrasonic frequencies [17,26,36,37]. However, the combined effect of frequency and glass bead size/amount with/without TiO_2 coating has not been previously investigated to determine H_2O_2 production. In addition, in most of the previous studies in sonocatalysis, experiments were carried out over a limited range of operating parameters such as frequency and glass bead size/amount. The objective of this study was to determine the effect of solid (both inert and TiO_2-coated glass beads) size and amount on H_2O_2 production at various frequencies in aqueous sonocatalytic environments.

2. Materials and methods

2.1. Materials

Glass beads of varying sizes (0.05 to 5 mm diameter) were purchased from Goryeo-Ace Inc., South Korea. The commercially available TiO_2-coated glass beads (5 mm diameter, anatase; ENB Korea Inc., South Korea) were employed as the catalyst. The chemicals used in this study, such as potassium hydrogen phthalate, potassium iodide, and ammonium molybdate, were of guaranteed reagent grade and did not require further purification. All sample solutions were prepared with ultrapure deionized (DI) water.

2.2. Sonocatalytic experiments

A schematic diagram of the experimental setup is shown in Fig. 1. The ultrasonic irradiation of the aqueous samples was performed in a 3000 mL stainless steel bath-type reactor (15 cm L × 10 cm W × 20 cm H) (Ul-Tech, Korea) at various frequencies of 28, 580, and 1000 kHz with applied power of 200 ± 3 W at a constant temperature of 20 ± 1 °C. 1000 mL of DI water was poured into the bath reactor connected to a temperature control unit (Thermo Haake, Germany). Experiments were performed in the presence and absence of inert glass beads of varying size (0.05, 0.1, 1, 2, 3, and 5 mm diameter) at various doses (10, 25, 50, 100, and 200 g L^{-1}) at 28, 580, and 1000 kHz and pH 6.5. The power density applied to the solution was 0.2 W mL^{-1}. Additional experiments were carried out with TiO_2 supported on glass beads under identical conditions at a dose of 100 g L^{-1}. Aliquots of 1.5 mL were withdrawn at each set interval of 10 min during the total irradiation time of 60 min. Most reported values are an average of triplicate experimental results.

The concentration of hydrogen peroxide formed during aqueous sonolysis was determined using the KI dosimetry method [14]. A sample of 1.5 mL was collected and 0.75 mL of 0.1 M potassium hydrogen phthalate was added to it. An iodide reagent of 0.75 mL (0.4 M potassium iodide, 0.06 M NaOH, and 10^{-4} M ammonium molybdate) was added at $t = 0$ min. The solution mixtures were allowed to stand for 2 min, and absorbance was then measured using a UV spectrophotometer (Hewlett Packard, Germany) at 350 nm. The method detection limit was 2.9 μM H_2O_2.

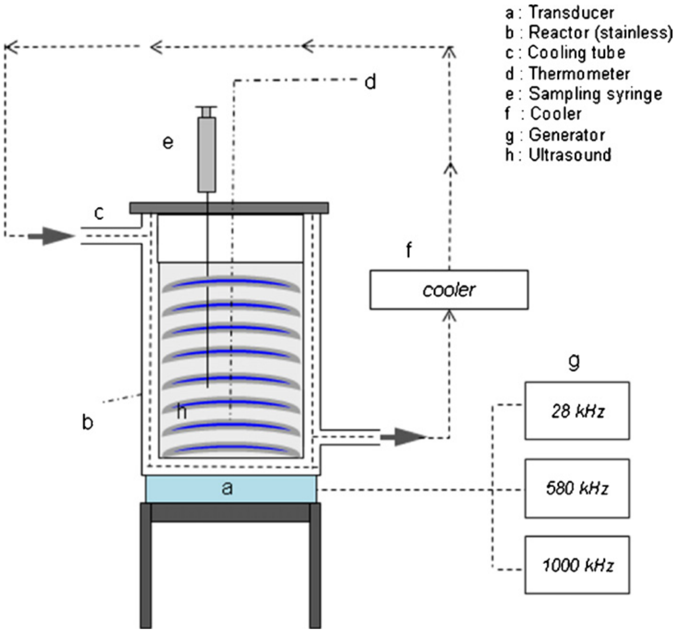

Fig. 1. Schematic of ultrasound system.

3. Results and discussion

3.1. H_2O_2 formation in the presence of inert glass beads

In order to investigate the effect of solid surfaces on ultrasonic reactivity, inert glass beads of varying size were added to aqueous samples at pH 6.5. H_2O_2 production was determined in the presence of various glass bead sizes ranging from no addition to 5 mm to investigate the efficacy of different sonochemical reactions in generating free radical species. It is widely accepted that H_2O_2 arises from the reaction of $HO^\bullet$ and $HOO^\bullet$ radicals in the liquid phase around a cavitational bubble and can thus be used to quantify the efficacy of reactors in generating the desired cavitational intensity [38]. The relative reactivity of ultrasound is compared in DI water at various frequencies of 28, 580, and 1000 kHz in Fig. 2. The concentration of H_2O_2 generated was found to increase linearly with ultrasonic irradiation time. The formation of H_2O_2 at a constant frequency was also found to be dependent on glass bead size, with the highest concentration produced in the 580 kHz reactor regardless of glass bead size. H_2O_2 production at different frequencies and 60 min contact time in the presence/absence of glass beads followed this order: 580 kHz (339 μM/no addition–105 μM/2 mm) > 1000 kHz (208 μM/no addition–4.0 μM/1 mm) > 28 kHz (71.2 μM/0.1 mm–18.5 μM/no addition). This trend is consistent with previous reports on the effect of frequency on sonochemistry reaction efficiency. In our previous study, the degradation of several phenolic compounds followed the same order in the absence of glass beads: 580 kHz (91–93%) > 1000 kHz (84–86%) > 28 kHz (17–34%) [39].

For the given frequencies of 580 and 1000 kHz, H_2O_2 production decreases in the presence of glass beads, except for the 3 mm glass bead (see Fig. 2). H_2O_2 production increases in the presence of 0.05 and 0.1 mm glass beads at 28 kHz and decreases in the presence of 1–5 mm glass beads under the same frequency condition. Previous studies have reported that the presence of solids and/or catalysts in aqueous systems increased the reactivity of sonochemistry [17,36,40]. An explanatory description of the formation and

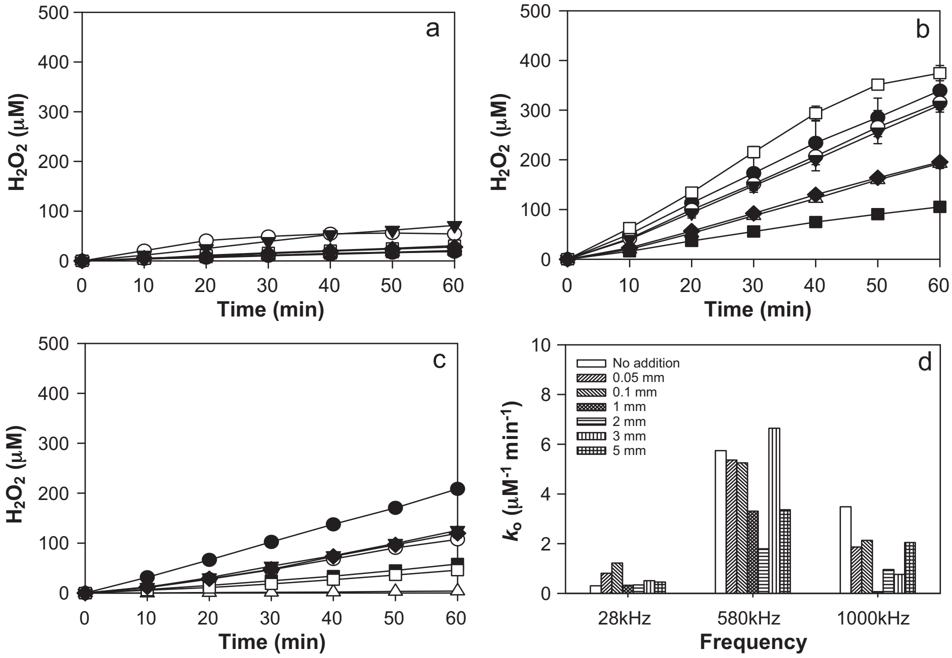

Fig. 2. Comparison of H_2O_2 production at (a) 28 kHz, (b) 580 kHz, and (c) 1000 kHz with inert glass beads. (d) Comparison of zero-order rate constants at various frequencies and bead sizes. Sonication conditions: 0.2 W mL^{-1}; 20 ± 1 °C; 100 g L^{-1} bead. Bead size: ●, no addition; ○, 0.05 mm; ▼, 0.1 mm; △, 1 mm; ■, 2 mm; □, 3 mm; ♦, 5 mm.

subsequent dynamic life of cavitation bubbles near a solid boundary in an acoustic field remains difficult. Fig. 3a shows the potential cavitation processes in the presence of glass beads at different frequencies in the four bubble collapses: (i) toroidal, (ii) spherical, (iii) symmetric, and (iv) asymmetric (microjet effect). The growth and collapse of cavitation bubbles in the acoustic system is influenced by ultrasound frequency, and the life cycles are very short. Except for frequencies in excess of a few MHz, theoretically, a cavitation bubble grows during the negative portion of the acoustic cycle and is forced to collapse during the positive portion [41]. For similar acoustic intensities and pressure amplitudes, cavitation bubbles at low frequencies (~20 kHz) grow for approximately 25 μs, while cavitation bubbles at high acoustic frequencies (~1 MHz) have only 0.5 μs of growth [42]. These significant differences in bubble growth result in small bubble sizes at high frequencies and consequently less violent collapses; approximately 10–50 μm at a low frequency of 28 kHz, 2.5–3.0 μm at a medium to high frequency of 580 kHz, and 1.5–2.0 μm at a high frequency of 1000 kHz, as shown in Fig. 2a [43–45].

Although it was assumed that the presence of solids would increase the reactivity of sonochemistry through the addition of inert glass beads, in this study, H_2O_2 production was not enhanced by the addition of various sizes of glass beads at the relatively high frequencies of 580 and 1000 kHz. The calculated wavelengths of ultrasound are approximately 53, 2.6, and 1.5 mm at 28, 580, and 1000 kHz, respectively. The general H_2O_2 production trend observed at 580 and 1000 kHz may occur because glass beads with similar sizes as the wavelengths interfere with the sonochemistry reaction, as shown in Fig. 3b. However, minimal interference in the reaction occurs in the presence of glass beads at 28 kHz, where the wavelength is significantly larger than the bead size. Sonochemical reactivity at this low frequency, as measured by zero-order rate constants for H_2O_2 production, was clearly proportional to the size of glass beads, 0.81 $\mu M^{-1}\ min^{-1}$ for 0.05 mm and 1.22 $\mu M^{-1}\ min^{-1}$ for 0.1 mm, while the rate constants (0.33–0.51 $\mu M^{-1}\ min^{-1}$) in the presence of the larger sizes of glass beads ranging from 1 to 5 mm were slightly higher than that for no addition (0.31 $\mu M^{-1}\ min^{-1}$) in Fig. 2.

For the solid surfaces, a previous study reported that a cavitation bubble collapse process was achieved in two acoustic cycles [46]: (i) a spherical bubble collapsed towards the solid boundary to its minimum volume and then rebounded and grew into a toroidal bubble (or two individual bubbles) in one acoustic cycle and (ii) a toroidal bubble (or two individual bubbles) collapsed towards the center of the ring to its minimum volume and then rebounded into a spherical bubble in the next acoustic cycle (Fig. 3a). Asymmetric bubble collapses with a vortex ring produce sonoluminescence in heterogeneous sonochemistry, which result in free radical production in the near vicinity of the solid surface, a rich region for sonochemical reactions [42]. The population (i.e., number and size) of cavitation bubbles depends on the frequency of irradiation. It is well known that lower irradiation frequencies produce a smaller number of cavitation bubbles, since bubbles grow to a greater extent and undergo higher compression [47]. At a low frequency, bubbles have relatively more time to grow and to collapse, which result in large maximum sizes and greater violent collapses. In our study, at the low frequency of 28 kHz, an assumption was made that the time available and the amount of water vapor during the growth phase of the cavitation bubbles could be expected to be higher in the presence of glass beads compared to no addition. Thus, an increase in H_2O_2 production could be expected as the glass bead is added.

To further investigate the effect of solid amounts on sonochemical reactivity, glass beads of varying solid amounts ranging from 0 to 200 g L^{-1} with a surface area of 41 $cm^2\ g^{-1}$ were added to aqueous systems. We focus on 0.1 mm glass bead for the solid amount effect study, since H_2O_2 production is highest with the addition of 100 g L^{-1} glass bead at 28 kHz in Fig. 2. The relative reactivity of sonochemistry in glass bead systems, quantified by H_2O_2 production, is compared in Fig. 4. For a given glass bead amount, the sonochemistry reactivity followed this order: 580 kHz > 1000 kHz > 28 kHz, however, H_2O_2 production varied significantly depending on the amount of glass bead at different frequencies. Sonochemical reactivity, as measured by zero-order rate constants for H_2O_2 production, was indirectly proportional to the amount (surface area) of glass beads at 28 kHz (Fig. 4). For the low frequency of 28 kHz, the zero-order rate constant is the

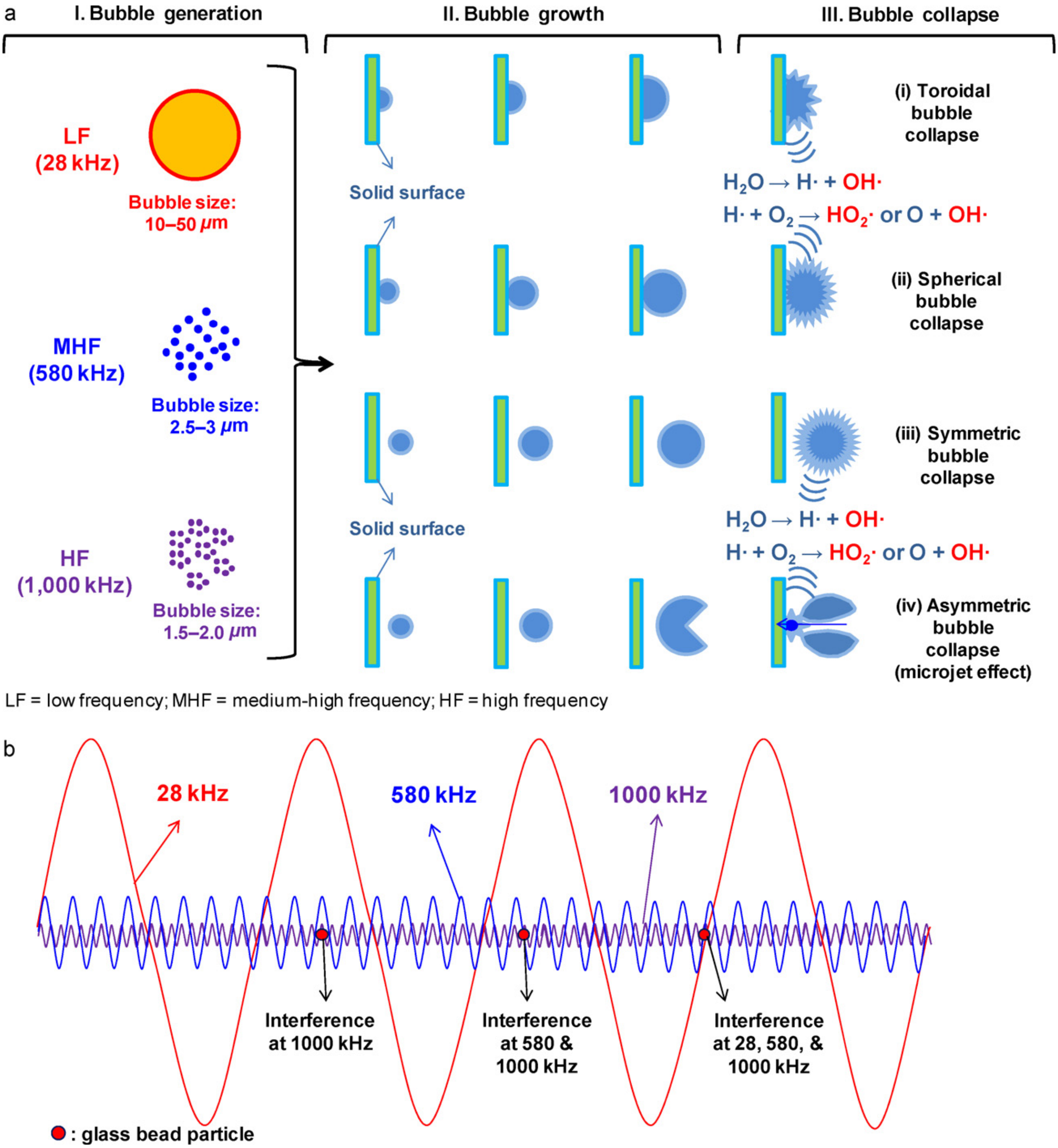

Fig. 3. Pattern of cavitation process: (a) four different collapse effects and (b) glass-bead interference at various frequencies.

highest in the presence of 10 g L^{-1} glass bead (3.3 μM^{-1} min^{-1}) and decreases significantly with increasing glass bead amounts (2.7 μM^{-1} min^{-1}/25 g L^{-1} to 0.45 μM^{-1} min^{-1}/200 g L^{-1}), while the rate constant is the lowest (0.31 μM^{-1} min^{-1}) with no addition. The sonochemistry reactivity at low frequency increases since, like superoxide [48], H_2O_2 can sorb on silica quartz surfaces; this sorption may play a role in the increased reactivity of H_2O_2 in the presence of glass bead. However, the glass bead amount threshold for the zero-order rate constant (7.9 μM^{-1} min^{-1}/50 g L^{-1}) at 580 kHz is significantly higher than that at 28 kHz, while the rate constant decreases in the entire range of glass beads at 1000 kHz. The results suggest that the amount (surface area) of the solid is responsible for increased and/or decreased sonochemical reactivity in solid-H_2O_2 systems. In the presence of glass beads, possible mechanisms of enhanced H_2O_2 reactivity include (i) catalytic effects at the solid surface, (ii) increased/decreased lifetime of H_2O_2 in the solid surface microenvironment, and (iii) changes in the salvation shell morphology of sorbed H_2O_2 [36]. In addition, H_2O_2 formation can be enhanced by increasing the bubble population in a standing wave field due to shorter intervals between the active regions corresponding to a decrease in the wavelength [49].

3.2. H_2O_2 formation in TiO_2-coated glass bead systems

Heterogeneous experiments were conducted in the presence of inert glass beads as described in the previous section. One size

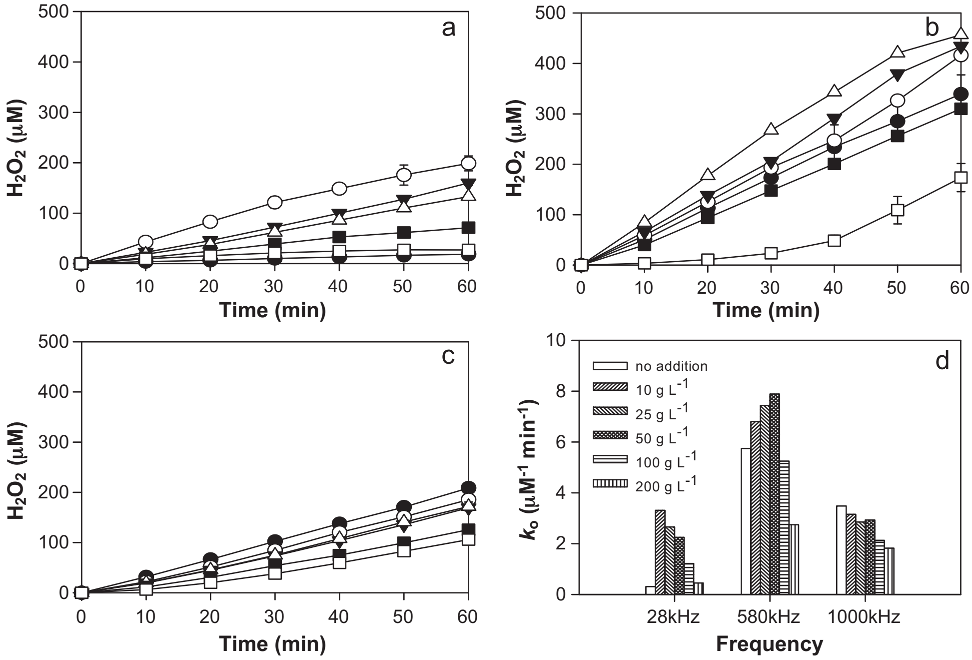

Fig. 4. Comparison of H_2O_2 production at (a) 28 kHz, (b) 580 kHz, and (c) 1000 kHz at varying inert glass bead amounts. (d) Comparison of zero-order rate constants at various frequencies and bead amounts. Sonication conditions: 0.2 W mL^{-1}; 20 ± 1 °C; 0.1 mm glass bead. Bead amount: ●, no addition; ○, 10 g L^{-1}; ▼, 25 g L^{-1}; △, 50 g L^{-1}; ■, 100 g L^{-1}; □, 200 g L^{-1}.

(5 mm) of inert and TiO_2-coated glass beads was further tested for 60 min sonocatalytic reactivity under a constant amount of the beads in a solution of 100 g L^{-1}. Fig. 5 shows that sonocatalysis with the addition of TiO_2-coated glass bead was found ineffective for H_2O_2 production at the high frequencies of 580 kHz (33.4 μM) and 1000 kHz (8.9 μM), while no addition and the addition of inert glass bead had somewhat constant sonochemical reactivity (297–340 μM at 580 kHz and 164–209 μM at 1000 kHz). Nevertheless, sonocatalysis with TiO_2-coated glass beads at the low frequency of 28 kHz was tremendously more effective (1540 μM) than that with no addition and inert glass beads (12–18 μM). The extraordinary effect of TiO_2 sonocatalysis is due to a variety of simple and complex factors. The simple reasons include: (i) the slightly positive character of the semiconductor surface at pH < 6.8 [50], at which the attractive forces between water molecules and the positively charged solid surfaces enhance the sonochemical reactivity; (ii) the turbulent flow conditions that facilitate mass transfer processes and chemical reactivity at the catalyst surface; and (iii) advantages of glass beads for the number of active reaction sites [37]. As briefly described previously, other technologies using

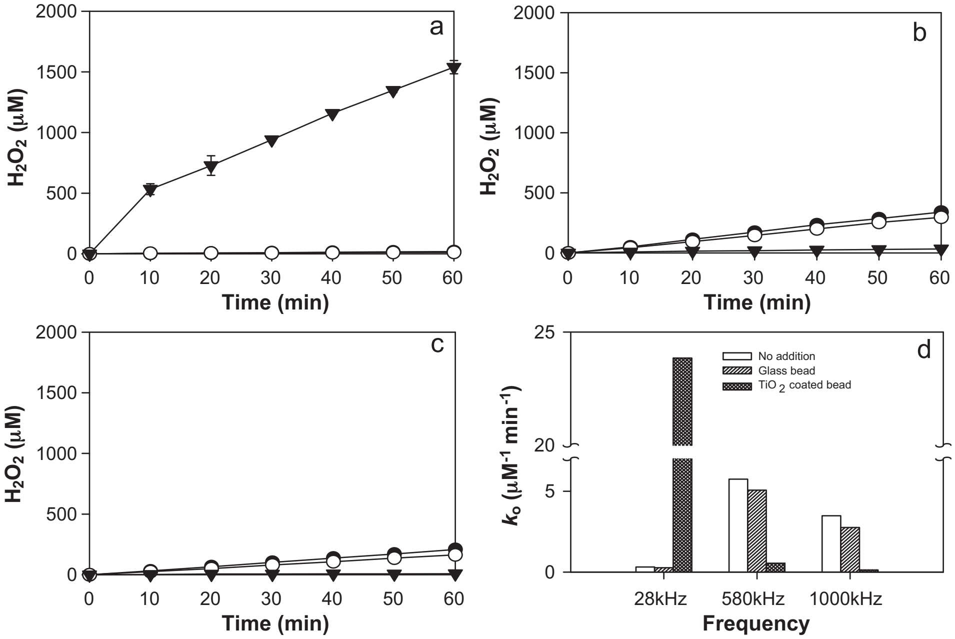

Fig. 5. Comparison of H_2O_2 production at (a) 28 kHz, (b) 580 kHz, and (c) 1000 kHz with TiO_2-coated glass beads. (d) Comparison of zero-order rate constants at various frequencies. Sonication conditions: 0.2 W mL^{-1}; 20 ± 1 °C; 100 g L^{-1} glass bead (5 mm). Bead: ●, no addition; ○, glass bead; ▼, TiO_2-coated glass bead.

a catalytic membrane contactor and photo-Fenton reactions that produce H_2O_2 (<1.2 to ~200 μM) can be used to remove different contaminants [20–22]. However, sonocatalysis with TiO_2-coated glass beads at the low frequency during this study that produces the very high concentration of H_2O_2 should be significantly more effective to degrade contaminants than those technologies, since sonochemical reactions associated with $OH^\bullet$ remove contaminants effectively in water.

The high efficacy for H_2O_2 production in the presence of TiO_2-coated glass bead is a result of the production of local "hot spots" upon implosion of some bubbles on the catalyst surface that leads to the formation of electron–hole pairs and excess $OH^\bullet$ [51]. Cavitation increases due to the heterogeneous nucleation of bubbles, resulting in the induction of hot spots in solution. Sonochemical reactions depend on the average bubble temperature and the number of active bubbles whereas sonoluminescence intensity depends on the maximum bubble temperature of the collapsing bubbles and the number of active bubbles [47]. In our study, the low frequency of 28 kHz led to an increase in the maximum size and formation rate of active bubbles in the presence of catalysis by providing additional nuclei. This can be expected to result in an increase in the maximum collapse temperature, which enhances the cavitation power and increases the pyrolysis of H_2O molecules and formation of $OH^\bullet$. At the low frequency, TiO_2-coated glass beads may not only promote the formation of $OH^\bullet$, but may also provide more stable reactive species for intensive oxidation [17]. Formations of TiO_3 on the surface of TiO_2 particles and H_2O_2 have been reported under ultrasonic irradiation [27]. At 20 kHz, sonoluminescence originates from chemoluminescence and plasma emissions of stable cavitation bubbles [52]. The intensity of such sonochemistry is sufficiently strong under high maximum bubble temperature and nonsymmetrical collapse conditions [53]. The formation of these reactive chemicals initiates a series of sonochemical reactions that may promote the power of oxidation. The high frequencies of 580 and 1000 kHz with TiO_2-coated glass bead showed significantly unsuccessful H_2O_2 formation compared to the low frequency of 28 kHz (Fig. 5). Determining how this occurs as a function of frequency is complex. Nevertheless, we simply assume that the TiO_2-coated glass beads (5 mm) that are of a larger size than those at the higher wavelengths (2.6 mm at 580 kHz and 1.5 mm at 1000 kHz) could potentially interfere with the sonochemistry reaction. The sonoluminescence intensity is also decreased significantly at higher irradiation frequencies as a result of several factors, such as a decrease in maximum bubble temperature, an increase in the amount of gaseous material within the bubbles, and a decrease in the number of active bubbles [47].

4. Conclusions

In this study, the effects of ultrasound frequency and inert/TiO_2-coated glass beads on H_2O_2 production were experimentally investigated. The results reveal that at the low frequency of 28 kHz, sonochemical reactivity increases in the presence of inert glass beads, since the presence of a heterogeneous catalyst seems to increase the formation rate of cavitation bubbles by providing additional nuclei [27,28]; this increases the pyrolysis of water molecules and the formation of hydroxyl radicals. However, no sonochemical enhancement was found at high frequencies (580 and 1000 kHz) in the presence of inert glass beads, excluding the 0.1 mm glass bead ($10–50\,g\,L^{-1}$), presumably since the relatively large glass beads having sizes similar to the wavelengths used could potentially interfere with the sonochemistry reaction. The remarkable effect of TiO_2-coated glass bead was observed to enhance H_2O_2 production at 28 kHz, with the highest concentration produced with the addition of $10\,g\,L^{-1}$.

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